

Effects of hydrostatic pressure on the magnetism and martensitic transition of Ni-Mn-In magnetic superelastic alloys

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We report magnetization and differential thermal analysis measurements as a function of pressure across the martensitic transition in magnetically superelastic Ni-Mn-In alloys. It is found that the properties of the martensitic transformation are significantly affected by the application of pressure. All transition temperatures shift to higher values with increasing pressure. The largest rate of temperature shift with pressure has been found for $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ as a consequence of its small entropy change at the transition. Such a strong pressure dependence of the transition temperature opens up the possibility of inducing the martensitic transition by applying relatively low hydrostatic pressures.

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The Ni-Mn based Heusler compounds with compositions close to the stoichiometric Ni_2MnX (with X being group IIIA-VA elements) have been shown to exhibit many functional properties such as magnetic shape memory [1], magnetic superelasticity [2], magnetocaloric effects [3] and magnetoresistance [4], which derive from the coupling between the martensitic transition and the magnetic order. In this family of alloys, magnetic moments are mainly confined to the Mn atoms. The exchange interaction between magnetic moments is long range and oscillatory, and is mediated by the conduction electrons. As a consequence, the magnetic properties of these alloys are sensitive to the distance between neighboring Mn atoms, and, indeed, different magnetic behavior has been reported for alloys with different X element. At the martensitic transition, the change in the lattice cell modifies the distance between Mn-atoms which can lead to antiferromagnetic interactions. Antiferromagnetic interactions are expected to be present in off-stoichiometric Ni-Mn- X compounds with X as Ga [5], Sn [6], In [7] and Sb [8].

In the present paper, we investigate the effect of hydrostatic pressure on Ni-Mn-In magnetic shape memory alloys. The application of pressure modifies the distance between Mn atoms thereby affecting the magnetic exchange. The relative stability between the high temperature cubic phase and the low temperature martensitic phase is also be affected by pressure.

Two samples were prepared by arc melting pure metals under argon atmosphere. They were then annealed

at 1073 K for 2 hours and quenched in ice-water. The compositions of the alloys were determined by energy dispersive x-ray analysis to be $\text{Ni}_{50.0}\text{Mn}_{34.0}\text{In}_{16.0}$ and $\text{Ni}_{49.5}\text{Mn}_{35.5}\text{In}_{15.0}$. Magnetization measurements were performed using a superconducting quantum interference device magnetometer equipped with pressure cell in fields up to 5 T in the temperature range 4 - 340 K and for pressures up to 10 kbar. High-pressure differential thermal analysis (HP-DTA) was carried out in a calorimeter capable of operating in the temperature and pressure ranges 183 - 473 K and 0 - 3 kbar respectively. The calorimeter is similar to that described in [9]. Powder samples were mixed with an inert perfluorinated liquid (Galden, from Bioblock Scientifics) before they were hermetically sealed in order to ensure pressure transmission. Thermal curves were recorded as a function of temperature for selected pressure values. HP-DTA scans were run on heating and cooling at 1 K min^{-1} rates.

Figure 1 shows the temperature dependence of the magnetization in a low external magnetic field of $H = 50 \text{ Oe}$ at selected applied pressures for $\text{Ni}_{50.0}\text{Mn}_{34.0}\text{In}_{16.0}$. Data have been taken in a zero-field-cooled (ZFC), field-cooled (FC), and field-heated (FH) sequence. Results for $p = 0$ agree with those previously reported [7]. On cooling, the cubic phase orders ferromagnetically at $T_C^A \simeq 310 \text{ K}$ which causes a sharp increase in the magnetization. At a lower temperature M_s , the sample transforms to the martensitic phase, and there is a sharp drop in the magnetization. Upon further cooling the magnetization rises again, reflecting the increase in ferromagnetic

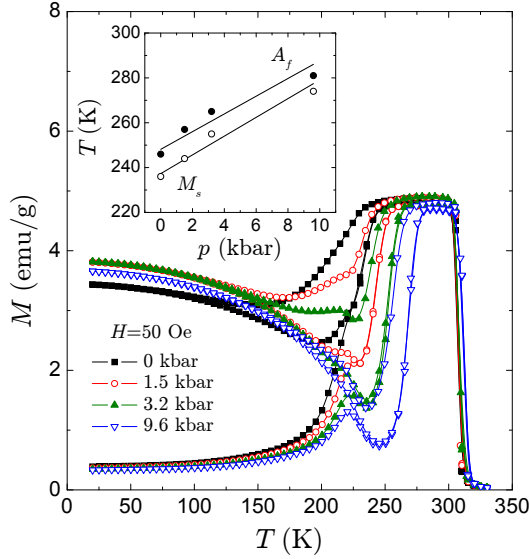


FIG. 1: (Color online) (a) Low field magnetization versus temperature curves for selected applied pressures. The inset shows the martensitic start transition temperature (M_s) and austenite finish temperature (A_f) as a function of the applied pressure.

order of the martensite at the Curie point of the martensitic phase T_C^M . The hysteresis in the FC and FH curves is a consequence of the first order character of the martensitic transition, while the splitting between ZFC and FH curves is associated with the presence of low temperature anisotropy together with any possible antiferromagnetic components existing in the martensitic state.

The application of pressure has little effect on the magnetic behavior of the high temperature cubic phase. Magnetization values below T_C^A are coincident within experimental error for all applied pressures. The T_C^A marginally increases with pressure, in agreement with data reported for related Heusler alloys [10, 11, 12] and are consistent with the predictions of first principles calculations [13]. Also, below about 150 K, well in the martensitic state, the temperature behavior of the magnetization remains nearly the same at all pressures. However, pressure has a significant effect on the magnetic behaviour in the temperature region where the austenitic and martensitic phases coexist. All characteristic temperatures associated with the martensitic transition shift to higher values as the pressure is increased. The inset in Fig. 1 shows the pressure dependence of M_s and A_f which exhibit similar behaviour with pressure. Another feature is that the change in the magnetization between martensite and austenite becomes larger with increasing pressure. Such an increase is consistent with the fact that the martensitic transition is shifted to higher temperatures, and along with this, the ferromagnetic order of the martensite decreases as the temperature increases. Also, application of pressure is expected to enhance any antiferromagnetic exchange present in the martensitic phase.

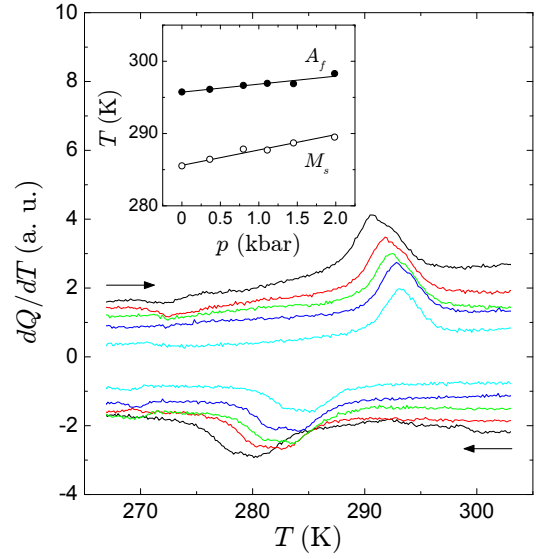


FIG. 2: (Color online) (a) DTA curves for selected values of applied pressure. From top to bottom (heating) and bottom to top (cooling) the applied pressures are: 0 kbar, 0.36 kbar, 0.80 kbar, 1.11 kbar and 1.45 kbar. The inset shows the martensitic start transition temperature (M_s) and austenite finish temperature (A_f) as a function of the applied pressure.

To gain further information on pressure effects on the martensitic transition, we have performed DTA measurements under pressure. The thermal curves for powder $\text{Ni}_{49.5}\text{Mn}_{35.5}\text{In}_{15.0}$ at selected hydrostatic pressures are shown in Fig. 2. The endothermic and exothermic peaks corresponding to the reverse and forward transitions on heating and cooling respectively are visible on the curves. Application of pressure does not significantly alter the shape of the thermal peak. For this sample, both forward and reverse transitions also shift towards higher temperatures as the pressure increases. The rate of shift in the transition temperatures in $\text{Ni}_{49.5}\text{Mn}_{35.5}\text{In}_{15.0}$ $dT/dp \approx 2$ K kbar $^{-1}$ is lower than in $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16.0}$ with $dT/dp \approx 4$ K kbar $^{-1}$.

For first order phase transitions, the shift in the transition temperatures is accounted for by the Clausius-Clapeyron equation $dT/dp = \Delta v / \Delta S$, where ΔS and Δv are respectively the entropy and volume changes at the phase transition. Complementary differential scanning calorimetry measurements have been performed which give $\Delta S = 2.17$ J mol $^{-1}$ K $^{-1}$ for $\text{Ni}_{49.5}\text{Mn}_{35.5}\text{In}_{15}$ and $\Delta S = 0.53$ J mol $^{-1}$ K $^{-1}$ for $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$. By using a molar volume of $v = 8.9$ m 3 mol $^{-1}$ for 15.0 at% In and $v = 9.2$ m 3 mol $^{-1}$ for 16 at% In computed from X-ray data, we obtain the relative volume changes at the martensitic transition of 0.6 % and 0.3 % for $\text{Ni}_{49.5}\text{Mn}_{35.5}\text{In}_{15.0}$ and $\text{Ni}_{50.0}\text{Mn}_{34.0}\text{In}_{16.0}$ respectively. The larger shift in the transition temperatures found for the 16 at% sample is due to its lower value of ΔS at the transition.

Figure 3 compares the shift in the martensitic transition temperature found for Ni-Mn-In alloys to those

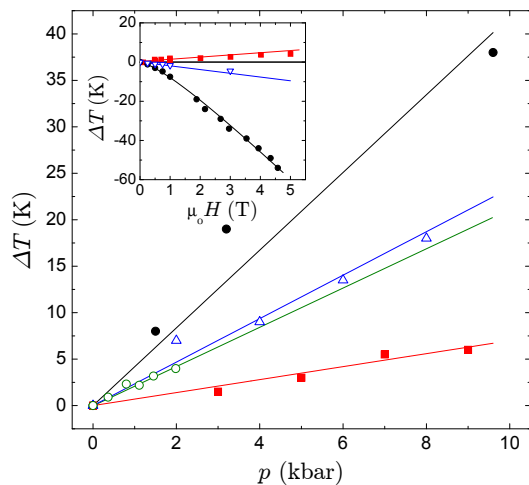


FIG. 3: (Color online) Shift with pressure of the martensitic transition temperature for $\text{Ni}_{53.5}\text{Mn}_{23}\text{Ga}_{23.5}$ (squares) [14], $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}$ (up triangles) [15], $\text{Ni}_{49.5}\text{Mn}_{35.5}\text{In}_{15}$ (open circles) and $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ (solid circles). Lines are fits to the data. The inset shows the shift in the transition temperature with magnetic field. Data correspond to the same samples than for the pressure dependence but for Ni-Mn-Sn, the line corresponds to $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}$ [15] while down triangles stand for $\text{Ni}_{50}\text{Mn}_{35}\text{Sn}_{15}$ [16].

reported for several Ni-Mn- X shape memory alloys [17]. In all cases, the martensitic transition temperature increases with increasing pressure as a consequence of the lower volume of the martensitic phase with respect to the cubic phase. For Ni-Mn-Ga alloys, the rate of change is smaller than for Ni-Mn-Sn and Ni-Mn-In. Such a difference is due to the fact that for this alloy, the relative

volume change is smaller [14] than for Ni-Mn-Sn [15] and Ni-Mn-In [18]. In magnetic shape memory alloys, the coupling between magnetism and structure results in a magnetic field dependence of the structural transition. The inset in Fig. 3 shows the magnetic field dependence of the martensitic transition temperature for the same samples for which data are shown in Fig. 3. For Ni-Mn-Ga, there is a slight increase in the transition temperature with increasing magnetic field, while in Ni-Mn-Sn and Ni-Mn-In, the transition temperatures decrease with increasing field. Such different behavior is due to the fact that the saturation magnetization of the martensitic phase is larger than that of the austenite in Ni-Mn-Ga while for Ni-Mn-Sn and Ni-Mn-In, the martensitic state has a lower magnetization than the austenitic state. We note that the rate of change in the transition temperature with both pressure and magnetic field for the sample with 16 at% In is much larger than in other Ni-Mn- X alloys. Such behavior is due to the lower entropy change in this alloy as compared to the entropy change in the other alloys. Therefore, for this alloy, it is easier to induce the martensitic transition by applying moderate hydrostatic pressure or magnetic field as opposed to the other compounds. This feature opens up a broad range of possible applications of the functional properties of this alloy, such as magnetic superelasticity, caloric effects, magnetoresistance, etc., associated with a pressure or magnetic field induced martensitic transition.

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